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Abstract

Near-UV irradiation of $Ru(CO)_4(\eta^2$-1,4-pentadiene), formed from visible light (λ> 420 nm) irradiation of $Ru_3(CO)_{12}$, in alkane solution containing excess 1,4-pentadiene at 298 K yields $Ru(CO)_3(\eta^4$-1,4-pentadiene) even in the presence of ~1 M 1,4-pentadiene. The complex $Ru(CO)_3(\eta^4$-1,4-pentadiene) isomerizes to the thermodynamically more stable conjugated diene complex, $Ru(CO)_3(\eta^4$-1,3-pentadiene) with a half-time of about 2 minutes at 298 K. Near-UV irradiation of $Ru(CO)_4(\eta^2$-1,4-pentadiene) in rigid methylcyclohexane glasses containing ~1 M 1,4-pentadiene at 77 K yields $Ru(CO)_3(\eta^4$-1,4-pentadiene) as the major product (~75%), but $HRu(CO)_3(\eta^3$-$C_5H_7)$ is also observed as a minor product (~25%) which isomerizes to $Ru(CO)_3(\eta^4$-1,3-pentadiene) above 198 K. Room temperature photolysis of $Ru(CO)_4(\eta^2$-3-methyl-1,4-pentadiene) ~~in the~~ presence of 3-methyl-1,4-pentadiene gives $Ru(CO)_3(\eta^4$-3-methyl-1,4-pentadiene) and this species reacts to give a 1,3-diene complex with a half-time of >3 h. Near-UV irradiation of $Ru(CO)_4(\eta^2$-1,5-hexadiene) in the presence of ~1 M 1,5-hexadiene yields the non-conjugated diene complex, $Ru(CO)_3(\eta^4$-1,5-hexadiene). In contrast to $Ru(CO)_3(\eta^4$-1,4-pentadiene), $Ru(CO)_3(\eta^4$-1,5-hexadiene) is stable for hours in alkane solution at 298 K. Near-UV irradiation of $Ru(CO)_4(\eta^2$-1,6-heptadiene) in the presence of ~1 M 1,6-heptadiene does not generate a chelating diene complex $Ru(CO)_3(\eta^4$-1,6-heptadiene) but rather the bis-olefin

complex $Ru(CO)_3(\eta^2$-1,6-heptadiene$)_2$. Thermal reaction of $Ru(CO)_3(C_2H_4)_2$ with ~1 M diene = 1,4-pentadiene, 3-methyl-1,4-pentadiene, 1,5-hexadiene and 1,6-heptadiene yields the same products as observed from photolysis of $Ru(CO)_4(\eta^2$-diene) in ~1 M diene at 298 K.

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Thermal Reactions of $Ru(CO)_3(C_2H_4)_2$ with Acyclic, Non-conjugated Dienes and Photochemistry of $Ru(CO)_4(\eta^2\text{-diene})$ Complexes

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<u>Abstract</u>

Near-UV irradiation of $Ru(CO)_4(\eta^2\text{-}1,4\text{-pentadiene})$, formed from visible light (λ> 420 nm) irradiation of $Ru_3(CO)_{12}$, in alkane solution containing excess 1,4-pentadiene at 298 K yields $Ru(CO)_3(\eta^4\text{-}1,4\text{-pentadiene})$ even in the presence of ~1 <u>M</u> 1,4-pentadiene. The complex $Ru(CO)_3(\eta^4\text{-}1,4\text{-pentadiene})$ isomerizes to the thermodynamically more stable conjugated diene complex, $Ru(CO)_3(\eta^4\text{-}1,3\text{-pentadiene})$ with a half-time of about 2 minutes at 298 K. Near-UV irradiation of $Ru(CO)_4(\eta^2\text{-}1,4\text{-pentadiene})$ in rigid methylcyclohexane glasses containing ~1 <u>M</u> 1,4-pentadiene at 77 K yields $Ru(CO)_3(\eta^4\text{-}1,4\text{-pentadiene})$ as the major product (~75%), but $HRu(CO)_3(\eta^3\text{-}C_5H_7)$ is also observed as a minor product (~25%) which isomerizes to $Ru(CO)_3(\eta^4\text{-}1,3\text{-pentadiene})$ above 198 K. Room temperature photolysis of $Ru(CO)_4(\eta^2\text{-}3\text{-methyl-}1,4\text{-pentadiene})$ in the presence of 3-methyl-1,4-pentadiene gives $Ru(CO)_3(\eta^4\text{-}3\text{-methyl-}1,4\text{-pentadiene})$ and this species reacts to give a 1,3-diene complex with a half-time of >3 h. Near-UV irradiation of $Ru(CO)_4(\eta^2\text{-}1,5\text{-hexadiene})$ in the presence of ~1 <u>M</u> 1,5-hexadiene yields the non-conjugated diene complex, $Ru(CO)_3(\eta^4\text{-}1,5\text{-hexadiene})$. In contrast to $Ru(CO)_3(\eta^4\text{-}1,4\text{-pentadiene})$, $Ru(CO)_3(\eta^4\text{-}1,5\text{-hexadiene})$ is stable for hours in alkane solution at 298 K. Near-UV irradiation of $Ru(CO)_4(\eta^2\text{-}1,6\text{-heptadiene})$ in the presence of ~1 <u>M</u> 1,6-heptadiene does not generate a chelating diene complex $Ru(CO)_3(\eta^4\text{-}1,6\text{-heptadiene})$ but rather the bis-olefin

complex $Ru(CO)_3(\eta^2\text{-1,6-heptadiene})_2$. Thermal reaction of $Ru(CO)_3(C_2H_4)_2$ with ~1 M diene = 1,4-pentadiene, 3-methyl-1,4-pentadiene, 1,5-hexadiene and 1,6-heptadiene yields the same products as observed from photolysis of $Ru(CO)_4(\eta^2\text{-diene})$ in ~1 M diene at 298 K.

We wish to report the photochemistry of $Ru(CO)_4(\eta^2$-diene) (diene = 1,4-pentadiene, 3-methyl-1,4-pentadiene, 1,5-hexadiene, 1,6-heptadiene) complexes and the thermal reaction of $Ru(CO)_3(C_2H_4)_2$ with these dienes. We[1-4] and others[5-9] have previously reported the photochemical generation of catalytic intermediates at low temperatures as a means of investigating reactions of alkene complexes. In particular, we examined the photoassisted alkene isomerization catalysts derived from $Fe(CO)_5$ and $Ru_3(CO)_{12}$.[10-13] The key intermediate, $HM(CO)_3(\eta^3\text{-}C_3H_5)$, can be observed spectroscopically in a low temperature matrix.[1,4] However, the absence of synthetic routes to $M(CO)_n$(non-conjugated diene) complexes has hindered mechanistic studies of transition metal carbonyl catalyzed isomerization of non-conjugated dienes. An attempted synthesis that we tried, near-UV irradiation of an alkane solution of $Ru_3(CO)_{12}$ and 1,4-pentadiene, yields $Ru(CO)_3$(1,3-pentadiene) without build-up of the intermediate(s). $Ru(CO)_3$(1,5-cyclooctadiene) undergoes reaction with 1,4-pentadiene at 100 °C to give directly $Ru(CO)_3$(1,3-pentadiene).[14] Thus, both pathways to form pentadiene complexes yield isomerization of the 1,4-diene to give a conjugated diene complex.

Here, we report the use of $Ru(CO)_3(C_2H_4)_2$[1] as a "$Ru(CO)_3$" transfer reagent permitting preparation of the new, thermally labile complexes, $Ru(CO)_3(\eta^4$-1,4-pentadiene), $Ru(CO)_3(\eta^4$-3-methyl-1,4-pentadiene) and

$Ru(CO)_3(\eta^4$-1,5-hexadiene), equation (1). The η^4-diene

$$Ru(CO)_3(C_2H_4)_2 + \text{diene} \xrightarrow{298K} Ru(CO)_3(\eta^4\text{-diene}) \quad (1)$$

complexes are reactive. For example, $Ru(CO)_3(\eta^4$-1,4-pentadiene) isomerizes rapidly at 298 K to $Ru(CO)_3(\eta^4$-1,3-pentadiene) probably via $Ru(CO)_3(\eta^2$-1,4-pentadiene). The complexes $Ru(CO)_3(\eta^4$-1,4-pentadiene), $Ru(CO)_3(\eta^4$-3-methyl-1,4-pentadiene), and $Ru(CO)_3(\eta^4$-1,5-hexadiene) can also be obtained by near-UV irradiation of $Ru(CO)_4(\eta^2$-diene) in alkane solution at 298 K. The $Ru(CO)_4(\eta^2$-diene) complexes can be cleanly made with excess diene via visible light ($\lambda >$ 420 nm) photolysis of $Ru_3(CO)_{12}$ where $Ru(CO)_4(\eta^2$-diene) does not absorb, equation (2).

$$Ru_3(CO)_{12} + \text{diene} \xrightarrow{h\nu} 3\ Ru(CO)_4(\eta^2\text{-diene}) \quad (2)$$

Experimental

Materials. All solvents were reagent grade and freshly distilled before use. The $Ru_3(CO)_{12}$ was obtained from Strem Chemicals and was used as received. The photochemistry at low temperature was carried out using methylcyclohexane (J.T. Baker) as the matrix material. The 1,3-pentadiene, 1,4-pentadiene, 3-methyl-1,4-pentadiene, 1,5-hexadiene, and 1,6-heptadiene were obtained from Aldrich and passed through Al_2O_3 prior to use. Research grade C_2H_4 was obtained from Matheson. The PPh_3 was recrystallized prior to use.

Instrumentation. IR spectra were recorded using a Nicolet 7199 or 60SX Fourier transform IR spectrometer. UV-VIS spectra were recorded using a Hewlett Packard 8451A Diode Array spectrometer. Gas chromatograph-mass spectra (GC-MS) were recorded on a Hewlett-Packard model 5992 mass spectrometer. All mass spectra were recorded at 70 ev. Separations were done using a 10 ft. x 1/8 in. SE-30 on chromasorb W column. A Model A High Energy Micro Pulser from Xenon Coorperation was used for flash photolysis. The pulser is equipped with the Xenon FP series of Micropulse Flashtubes used at a discharge voltage of ~5 kilovolts.

Procedures. Generally, all manipulations were carried out under N_2 in a Vacuum Atmospheres dry box or under Ar using conventional Schlenk line techniques. Low temperature irradiations involved the use of a Bausch and Lomb SP200 200 W high pressure Hg lamp filtered with a 10 cm Pyrex water filter. Low temperature IR spectra were recorded using a

Precision Cell, Inc. Model P/N 21.000 variable temperature cell equipped with CaF_2 windows.

Solutions of ~1 m$\underline{M}$ $Ru(CO)_3(C_2H_4)_2$ were prepared according to the literature procedure,[1] and all solutions of $Ru(CO)_3(C_2H_4)_2$ were saturated with C_2H_4 to prevent decomposition. In a typical procedure, the $Ru(CO)_4(C_2H_4)$ was prepared quantitatively via visible light ($\lambda >$ 420 nm) irradiation of 0.4 m$\underline{M}$ $Ru_3(CO)_{12}$ in a continuously C_2H_4-purged alkane solution using a filtered Hanovia 550 W medium pressure Hg lamp. The $Ru(CO)_3(C_2H_4)_2$ solution were prepared by subsequent near-UV irradiation of a $Ru(CO)_4(C_2H_4)$ solution at 298 K in the presence of C_2H_4. Only $Ru(CO)_4(C_2H_4)$ and $Ru(CO)_3(C_2H_4)_2$ were spectroscopically detected in these solutions. After ~90% conversion of $Ru(CO)_4(C_2H_4)$, the photolysis was stopped and the solution was purged with C_2H_4 to remove photogenerated CO. All thermal reactions with dienes according to equation (1) were carried out using freshly prepared solutions of $Ru(CO)_3(C_2H_4)_2$. IR data for complexes studied are found in Table I. In general we are not able to isolate the $Ru(CO)_n(olefin)_{5-n}$ (n = 4, 3) complexes or obtain clean NMR data, since these complexes are stable only in the presence of excess olefin.

$Ru(CO)_4(\eta^2$-1,4-pentadiene), $Ru(CO)_4(\eta^2$-3-methyl-1,4-pentadiene), $Ru(CO)_4(\eta^2$-1,5-hexadiene), and $Ru(CO)_4(\eta^2$-1,6-heptadiene) were prepared via a modification of the preparation for $Ru(CO)_4(C_2H_4)$. Visible light ($\lambda >$ 420 nm)

irradiation of ~0.4 m$\underline{M}$ $Ru_3(CO)_{12}$ in a 3-methylpentane solution containing ~1 $\underline{M}$ diene at 298 K cleanly yields $Ru(CO)_4(\eta^2$-diene).

Results and Discussion

(a) Thermal reaction of $Ru(CO)_3(C_2H_4)_2$ with 1,4-Pentadiene and 3-methyl-1,4-pentadiene. Addition of 1,4-pentadiene to a concentration of ~1 M to an alkane/C_2H_4 solution of ~1 mM $Ru(CO)_3(C_2H_4)_2$, at 298 K leads to rapid IR spectral changes which are consistent with the substitution reaction represented by equation (3). The difference IR spectra in

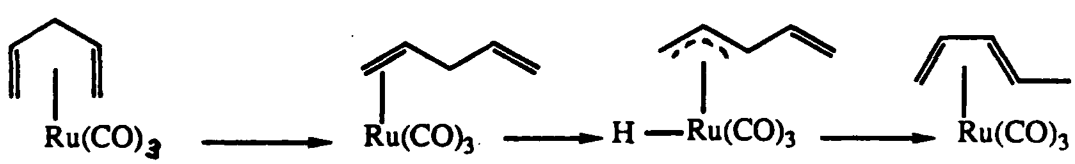
$$Ru(CO)_3(C_2H_4)_2 + \text{1,4-pentadiene} \xrightarrow{298K} Ru(CO)_3(\eta^4\text{-1,4-pentadiene}) \qquad (3)$$

Figure 1 show that the three absorption bands in the CO stretching region due to $Ru(CO)_3(C_2H_4)_2$ decrease in intensity immediately upon mixing, and two new bands at 2050, and 1966 cm^{-1} increase in intensity. The 2050, 1966 cm^{-1} bands in the IR spectrum differ from those observed for $Ru(CO)_3(\text{alkene})_2$, $Ru(CO)_3(\eta^4\text{-1,3-diene})$, and $HRu(CO)_3(\eta^3\text{-allyl})$, Table I. We assign the bands at 2050 and 1966 cm^{-1} to the complex, $Ru(CO)_3(\eta^4\text{-1,4-pentadiene})$. The $Ru(CO)_3(\eta^4\text{-1,4-pentadiene})$ complex has a third CO stretching band at 1992 cm^{-1}, which is obscured in the difference IR spectra by the band at 1995 cm^{-1} due to $Ru(CO)_3(C_2H_4)_2$.

As reported earlier,[1] $Ru(CO)_3(C_2H_4)_2$ reacts rapidly with L (L = CO, PPh_3, alkene) yielding $Ru(CO)_3(L)_2$. However, there are no bands attributable to $Ru(CO)_3(\eta^2\text{-1,4-pentadiene})_2$ in the IR spectrum from the reaction of

$Ru(CO)_3(C_2H_4)_2$ and ~1 M 1,4-pentadiene. We attribute the lack of formation of $Ru(CO)_3(\eta^2\text{-1,4-pentadiene})_2$ to the ability of 1,4-pentadiene to bind preferentially as a chelating ligand. Despite the thermodynamic chelate effect, the diene ligand in an alkane solutions of $Ru(CO)_3(\eta^4\text{-1,4-pentadiene})$ is very rapidly replaced by reaction with 0.05 M PPh_3 yielding $Ru(CO)_3(PPh_3)_2$ within 1 min.

As shown in Figure 1, $Ru(CO)_3(\eta^4\text{-1,4-pentadiene})$ isomerizes with a half-time of about 2 min at 298 K to give $Ru(CO)_3(\eta^4\text{-1,3-pentadiene})$ having bands at 2063, 1998, and 1987 cm^{-1}. The structure of this complex is assigned by comparison of IR and GC-mass spectral data with that from an authentic sample prepared independently by reaction of $Ru(CO)_3(C_2H_4)_2$ and 1,3-pentadiene. We presume[15] that the isomerization of the 1,4-pentadiene occurs via dechelation of the diene, oxidative addition of an allylic C-H bond yielding a π-allyl hydride complex followed by reductive elimination of a new allylic C-H bond, equation (4).



(4)

Light-induced loss of CO from $Ru(CO)_4(\eta^2\text{-1,4-pentadiene})$ can also yield the presumed coordinatively unsaturated η^2-

1,4-pentadiene intermediate and ultimately does yield the conjugated diene product (vide infra). Furthermore, low temperature photochemical experiments with $Ru(CO)_4(\eta^2$-1,4-pentadiene), vide infra, have been used to detect the π-allyl hydride intermediate.

Similar to 1,4-pentadiene, addition of ~1 M 3-methyl-1,4-pentadiene to an alkane/C_2H_4 solution of ~1 mM $Ru(CO)_3(C_2H_4)_2$ at 298 K also results in the rapid decline of IR spectral features for $Ru(CO)_3(C_2H_4)_2$ and growth of new features attributed to $Ru(CO)_3(\eta^4$-3-methyl-1,4-pentadiene), Figure 2a. The three CO stretching bands at 2052, 1994, and 1968 cm^{-1} for $Ru(CO)_3(\eta^4$-3-methyl-1,4-pentadiene) are remarkable similar to those for $Ru(CO)_3(\eta^4$-1,4-pentadiene), Table I. $Ru(CO)_3(\eta^4$-3-methyl-1,4-pentadiene) isomerizes with a half-time of >3 h at 298 K to $Ru(CO)_3(\eta^4$-3-methyl-1,3-pentadiene), Figure 2b. The slow isomerization of $Ru(CO)_3(\eta^4$-3-methyl-1,4-pentadiene) compared to $Ru(CO)_3(\eta^4$-1,4-pentadiene) is probably not only due to the replacement of one doubly-allylic hydrogen by a methyl group but is also due to steric hindrance associated with the methyl substituent in formation of a π-allyl hydride intermediate.

(b) Photoreaction of $Ru(CO)_4(\eta^2$-1,4-pentadiene) and $Ru(CO)_4(\eta^2$-3-methyl-1,4-pentadiene) at 298 K. The complex $Ru(CO)_4(\eta^2$-1,4-pentadiene) can be made via visible (λ> 420 nm) irradiation of an alkane solution of $Ru_3(CO)_{12}$ at 298 K, equation (2). The complex $Ru(CO)_4(\eta^2$-1,4-pentadiene) is, however, only stable in the presence of an excess of 1,4-

pentadiene (1 M is typically used). The selective irradiation of $Ru_3(CO)_{12}$ is a general and efficient way to synthesize $Ru(CO)_4(\eta^2$-olefin) (olefin = C_2H_4, C_3H_6, C_5H_{10}, 1,3-pentadiene, 1,4-pentadiene, 3-methyl-1,4-pentadiene, 1,5-hexadiene, 1,6-heptadiene), Table I. Owing to thermodynamic considerations, it is logical to conclude that all of the η^2-diene complexes involve the terminal double bond,[16] but this has not been unambiguously established.

Xenon flash (~50 μs) photolysis of ~1 mM $Ru(CO)_4(\eta^2$-1,4-pentadiene) in a 3-methylpentane solution at 298 K containing ~1 M 1,4-pentadiene yields $Ru(CO)_3(\eta^4$-1,4-pentadiene) via light-induced loss of CO, equation (5), Figure 3a. The difference IR spectrum of $Ru(CO)_3(\eta^4$-1,4-

$$Ru(CO)_4(\eta^2\text{-1,4-pentadiene}) \xrightarrow[\text{1,4-pentadiene}]{h\nu,\ 298K} Ru(CO)_3(\eta^4\text{-1,4-pentadiene}) + CO \qquad (5)$$

pentadiene) associated with this reaction shows the same bands for product as observed in the thermal reaction of $Ru(CO)_3(C_2H_4)_2$ with 1,4-pentadiene, Figure 1, except that the peak at 1992 cm^{-1} for $Ru(CO)_3(\eta^4$-1,4-pentadiene) is less obscured by the peak at 1994 cm^{-1} of $Ru(CO)_4(\eta^2$-1,4-pentadiene). The complex $Ru(CO)_3(\eta^4$-1,4-pentadiene) isomerizes to $Ru(CO)_3(\eta^4$-1,3-pentadiene) as discussed above with a half-time of ~2 min at 298 K. Figure 3b shows IR spectral data for the isomerization reaction. The data reveal that both the $Ru(CO)_3(\eta^4$-1,4-pentadiene) and

$Ru(CO)_3(\eta^4$-1,3-pentadiene) complexes clearly have three CO absorption bands.

Xenon flash photolysis of ~1 mM $Ru(CO)_4(\eta^2$-3-methyl-1,4-pentadiene) in a 3-methylpentane solution at 298 K containing ~1 M 3-methyl-1,4-pentadiene yields $Ru(CO)_3(\eta^4$-3-methyl-1,4-pentadiene) which shows the same bands as observed in thermal reaction of $Ru(CO)_3(C_2H_4)_2$ with 3-methyl-1,4-pentadiene. The follow-up thermal isomerization of $Ru(CO)_3(\eta^4$-3-methyl-1,4-pentadiene) occurs with a half-time of >3 h, as found from studies begining with $Ru(CO)_3(C_2H_4)_2$.

(c) Photoreaction of $Ru(CO)_4(\eta^2$-1,4-pentadiene) in a methylcyclohexane glass. In order to observe the unstable intermediates associated with the chemistry in equations (4) and (5), we studied the photochemistry of $Ru(CO)_4(\eta^2$-1,4-pentadiene) in a methylcyclohexane matrix at 77 K. When ~1 mM $Ru(CO)_4(\eta^2$-1,4-pentadiene) is irradiated in a rigid 1,4-pentadiene-containing (~1 M) glass, bands characteristic of free CO (2132 cm^{-1}) and $Ru(CO)_3(\eta^4$-1,4-pentadiene) (2048, 1960 cm^{-1}) are observed in the IR spectra, Figure 4. The rigid glass precludes diffusion of the presumed $Ru(CO)_3(\eta^2$-1,4-pentadiene) intermediate, thus ruling out polynuclear species as photoproducts. The rigid glass will, however, allow association of the free double bond of the η^2-1,4-pentadiene ligand with the vacant coordination site resulting from loss of CO to give $Ru(CO)_3(\eta^4$-1,4-pentadiene). We have not observed any bands in the IR

spectra at 77 K assignable to $Ru(CO)_3(\eta^2$-1,4-pentadiene) which we presume to be the primary photoproduct. $Ru(CO)_3(\eta^2$-1,4-pentadiene) might be able to observed at temperatures lower than 77 K, since $Ru(CO)_3(C_2H_4)$ has been observed upon photolysis of $Ru(CO)_4(C_2H_4)$ in a 3-methylpentane glass at 55 K,[1] Table I. Also, we do not find $Ru(CO)_3(\eta^2$-1,4-pentadiene$)_2$ as a product which might be expected owing to the presence of excess 1,4-pentadiene. However, if the concentration of 1,4-pentadiene is increased from 1 M to 4 M, we do observe $Ru(CO)_3(\eta^2$-1,4-pentadiene$)_2$ as a product (~20%) at 77 K. This assignment is based on IR spectral similarity to $Ru(CO)_3(C_2H_4)_2$ and other bis-olefin complexes, Table I.

There are important bands at 2080 and 2006 cm^{-1} in the IR spectra recorded after photolysis of $Ru(CO)_4(\eta^2$-1,4-pentadiene) at 77 K due to a second product (~25%), Figure 4. Based on the similarity of the frequencies and relative intensities of these bands to those for the known complexes $HRu(CO)_3(\eta^3$-allyl) (allyl = C_3H_5, C_5H_9), we assign the bands at 2080 and 2006 cm^{-1} to the allyl hydride complex $HRu(CO)_3(\eta^3$-$C_5H_7)$, Table I. Evidently, association of the free olefin and oxidative addition of the allylic C-H bonds of the η^2-1,4-pentadiene ligand in the presumed primary photoproduct, $Ru(CO)_3(\eta^2$-1,4-pentadiene), are competitive processes in the photolysis of $Ru(CO)_4(\eta^2$-1,4-pentadiene) at 77 K.

Warming the matrix containing the photogenerated

$HRu(CO)_3(\eta^3\text{-}C_5H_7)$ to 195 K results in the loss of the bands due to $HRu(CO)_3(\eta^3\text{-}C_5H_7)$ and growth in bands for $Ru(CO)_3(\eta^4$-1,3-pentadiene). Bands due to photogenerated $Ru(CO)_3(\eta^4$-1,4-pentadiene) survive the warmup process to 195 K. Further warmup to 298 K yields quantitative formation of $Ru(CO)_3(\eta^4$-1,3-pentadiene). This experiment demonstrates that $HRu(CO)_3(\eta^3\text{-}C_5H_7)$ can be an intermediate in the photochemical formation of $Ru(CO)_3(\eta^4$-1,3-pentadiene) from $Ru(CO)_4(\eta^2$-1,4-pentadiene) and is chemically competent to be an intermediate in the thermal isomerization of $Ru(CO)_3(\eta^4$-1,4-pentadiene) to $Ru(CO)_3(\eta^4$-1,3-pentadiene).

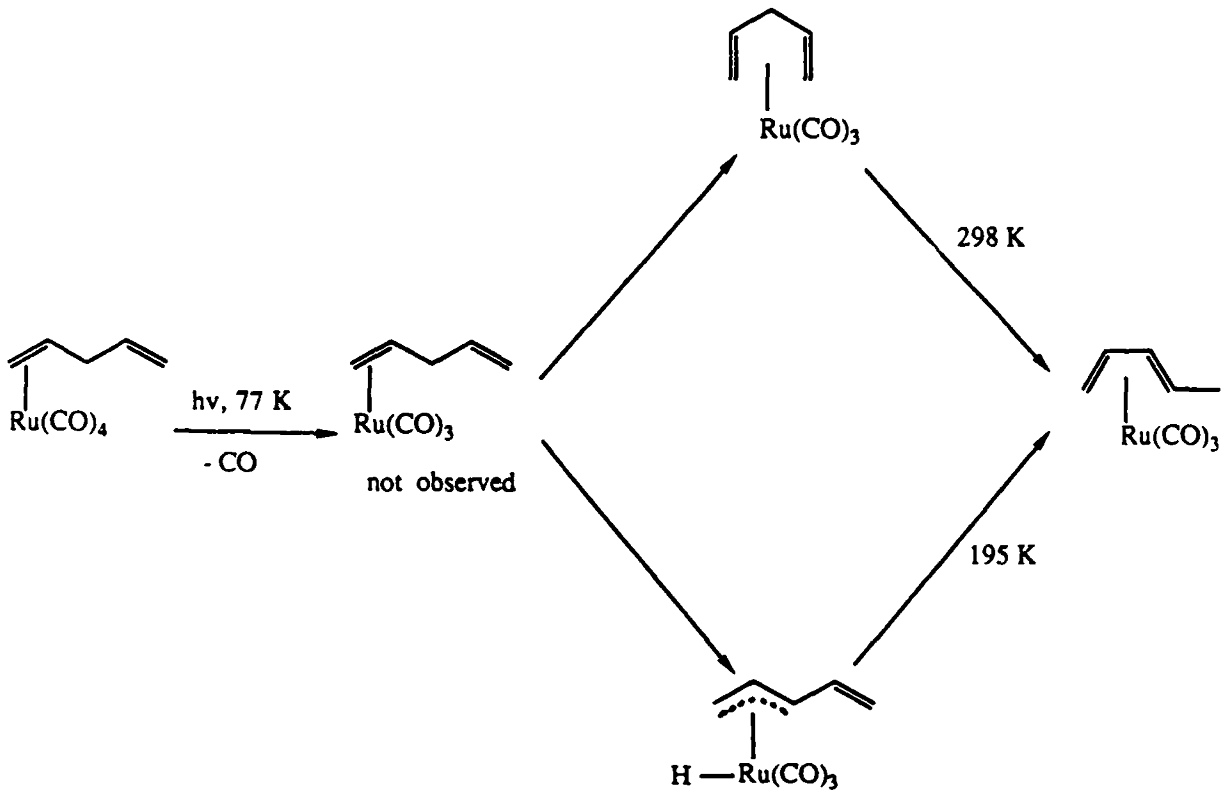
The photochemistry of $Ru(CO)_4(\eta^2$-1,4-pentadiene) in an alkane matrix at 77 K in the presence of excess 1,4-pentadiene and the thermal reaction of these intermediates when they are allowed to warm are summarized in Scheme I.

(d) Thermal reaction of $Ru(CO)_3(C_2H_4)_2$ with 1,5-hexadiene. Addition of 1 M 1,5-hexadiene to an alkane solution of 1 mM $Ru(CO)_3(C_2H_4)_2$ at 298 K results in IR spectral changes consistent with the substitution reaction represented by equation (6). Two new bands at 2050 and 1966 cm^{-1} appear in

$$Ru(CO)_3(C_2H_4)_2 + \text{1,5-hexadiene} \xrightarrow{298K} Ru(CO)_3(\eta^4\text{-1,5-hexadiene}) \qquad (6)$$

the IR spectra and the bands due to $Ru(CO)_3(C_2H_4)_2$ decrease in intensity immediately after addition of 1,5-hexadiene to

Scheme I. Photochemistry of $Ru(CO)_4(\eta^2\text{-}1,4\text{-pentadiene})$.



a solution of $Ru(CO)_3(C_2H_4)_2$, Figure 5. We assign the product in equation (6) to be $Ru(CO)_3(\eta^4$-1,5-hexadiene) based on its IR spectrum. The IR spectrum for the complex is remarkably similar to the IR spectra of $Ru(CO)_3(\eta^4$-1,4-pentadiene) and $Ru(CO)_3(\eta^4$-1,4-pentadiene), Table I. The coordinated 1,5-hexadiene in $Ru(CO)_3(\eta^4$-1,5-hexadiene) can also be replaced within 1 min at 298 K by reaction with 0.05 M PPh_3 yielding $Ru(CO)_3(PPh_3)_2$.

In contrast to $Ru(CO)_3(\eta^4$-1,4-pentadiene) or $Ru(CO)_3(\eta^4$-3-methyl-1,4-pentadiene), the complex $Ru(CO)_3(\eta^4$-1,5-hexadiene) is stable at 298 K in alkane solution under an inert atmosphere for hours. We attribute the rapid rate of isomerization of $Ru(CO)_3(\eta^4$-1,4-pentadiene) to $Ru(CO)_3(\eta^4$-1,3-pentadiene) to the presence of two doubly-allylic hydrogens in 1,4-pentadiene. Due to the steric effect of the methyl substituent on 3-methyl-1,4-pentadiene on the isomerization process $Ru(CO)_3(\eta^4$-3-methyl-1,4-pentadiene), with only one doubly-allylic hydrogen, shows a much slower rate of isomerization to $Ru(CO)_3(\eta^4$-3-methyl-1,3-pentadiene). Despite the substitution lability of $Ru(CO)_3(\eta^4$-1,5-hexadiene), it is surprisingly inert to isomerization. However, $Ru(CO)_3(C_2H_4)_2$ is not very active as an isomerization catalyst toward 1-pentene either, though the bis-1-pentene complex is very substitution labile.[1]

(e) Photoreaction of $Ru(CO)_4(\eta^2$-1,5-hexadiene) at 298 K. Flash photolysis of 1 mM $Ru(CO)_4(\eta^2$-1,5-hexadiene) in a 3-

methylpentane solution at 298 K containing 1 M 1,5-hexadiene leads to IR spectral changes which are consistent with the reaction represented by equation (7). The difference IR spectrum in Figure 6 shows that the three bands for

$$Ru(CO)_4(\eta^2\text{-1,5-hexadiene}) \xrightarrow[\text{1,5-hexadiene}]{h\nu,\ 298K} Ru(CO)_3(\eta^4\text{-1,5-hexadiene}) + CO \qquad (7)$$

$Ru(CO)_4(\eta^2$-1,5-hexadiene) decrease, and two new bands at 2050 and 1966 cm^{-1} increase in intensity. The positions of these bands are the same as those observed in the thermal reaction of $Ru(CO)_3(C_2H_4)_2$ with 1,5-hexadiene.

(f) Thermal reaction of $Ru(CO)_3(C_2H_4)_2$ with 1,6-heptadiene. Addition of ~1 M 1,6-heptadiene to an alkane solution of ~1 mM $Ru(CO)_3(C_2H_4)_2$ at 298 K results in IR spectral changes consistent with the substitution reaction represented by equation (8). The difference IR spectra in Figure 7 show

$$Ru(CO)_3(C_2H_4)_2 + \text{1,6-heptadiene} \xrightarrow{298K} Ru(CO)_3(\eta^2\text{-1,6-heptadiene})_2 \qquad (8)$$

that the three CO absorption bands due to $Ru(CO)_3(C_2H_4)_2$ decrease in intensity immediately upon mixing, and new bands at 2074 and 1986 cm^{-1} attributed to $Ru(CO)_3(\eta^2$-1,6-heptadiene$)_2$ increase in intensity. This assignment of the product is based on the spectral similarity to bis-C_2H_4 complex and other bis-olefin complexes. The shift to lower

frequencies is consistent with the substitution of C_2H_4 by 1,6-heptadiene, Table I. Interestingly, the product obtained from the reaction of $Ru(CO)_3(C_2H_4)_2$ and 1,6-heptadiene is not $Ru(CO)_3(\eta^4$-1,6-heptadiene) but $Ru(CO)_3(\eta^2$-1,6-heptadiene$)_2$. The reactivity difference between 1,6-heptadiene and the 1,4- and 1,5-dienes with $Ru(CO)_3(C_2H_4)_2$ is presumably due to the fact that the two double bonds of 1,6-heptadiene are too far apart for a cooperative chelate effect. $Ru(CO)_3(\eta^2$-1,6-heptadiene$)_2$ reacts with 0.05 M PPh_3 at 298 K yielding $Ru(CO)_3(PPh_3)_2$ within 1 min, demonstrating that it too is a very labile complex.

(g) Photochemistry of $Ru(CO)_4(\eta^2$-1,6-heptadiene) at 298 K. Xenon flash photolysis of $Ru(CO)_4(\eta^2$-1,6-heptadiene) in an alkane solution containing 1 M 1,6-heptadiene results in the formation of $Ru(CO)_3(\eta^2$-1,6-heptadiene$)_2$, equation (9).

$$Ru(CO)_4(\eta^2\text{-1,6-heptadiene}) \xrightarrow[\text{1,6-heptadiene}]{h\nu,\ 298K} Ru(CO)_3(\eta^2\text{-1,6-heptadiene})_2 + CO \quad (9)$$

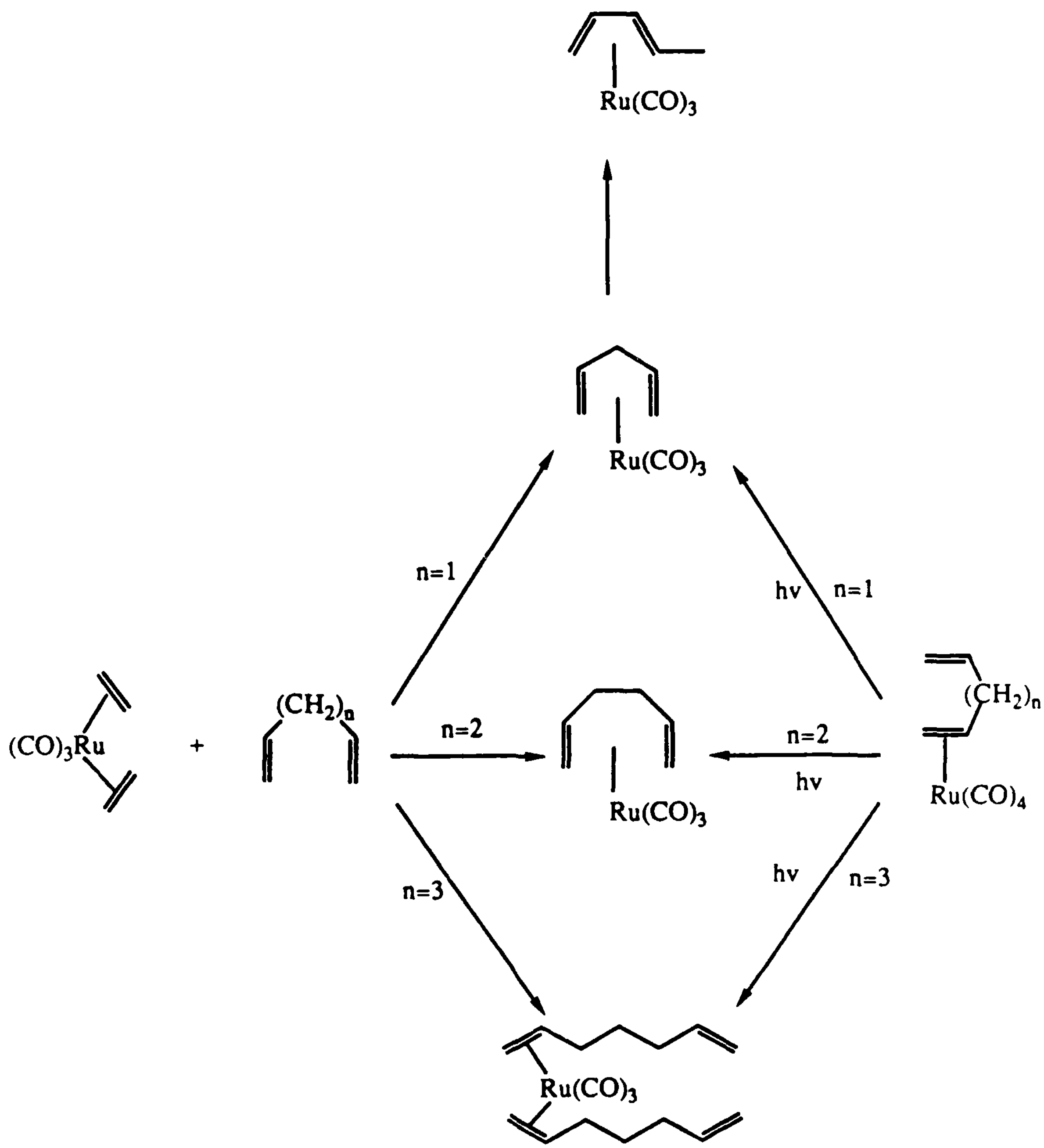
The IR spectrum of $Ru(CO)_3(\eta^2$-1,6-heptadiene$)_2$ produced in this reaction shows the same bands as observed in the thermal reaction of $Ru(CO)_3(C_2H_4)_2$ with 1,6-heptadiene.

Conclusions

As summarized in Scheme II, the photoreaction of $Ru(CO)_4(\eta^2$-diene) and the thermal reaction of $Ru(CO)_3(C_2H_4)_2$ with the diene give the same products. The products can be either $Ru(CO)_3(\eta^4$-diene) or $Ru(CO)_3(\eta^2$-diene$)_2$, depending on the number of saturated carbons between terminal double bonds. The chelation effect is significant for 1,4-pentadiene, 3-methyl-1,4-pentadiene, and 1,5-hexadiene, but 1,6-heptadiene does not form a chelate complex.

The presence of two doubly-allylic hydrogens in $Ru(CO)_3(\eta^4$-1,4-pentadiene) permits it to rapidly isomerize to $Ru(CO)_3(\eta^4$-1,3-pentadiene) at 298 K. Replacing one of the two doubly-allylic hydrogens by a methyl group significantly slows down the rate of isomerization at 298 K of $Ru(CO)_3(\eta^4$-3-methyl-1,4-pentadiene) to $Ru(CO)_3(\eta^4$-3-methyl-1,3-pentadiene). In contrast, $Ru(CO)_3(\eta^4$-1,5-hexadiene) is stable for several hours under the same conditions. We are not able to observe $Ru(CO)_3(\eta^2$-1,4-pentadiene) on irradiation of $Ru(CO)_4(\eta^2$-1,4-pentadiene) at 77 K. The significant products at 77 K are $Ru(CO)_3(\eta^4$-1,4-pentadiene) and $HRu(CO)_3(\eta^3$-$C_5H_7)$ which isomerizes to $Ru(CO)_3(\eta^3$-1,4-pentadiene) above 195 K. Thus, low temperature photochemistry of $Ru(CO)_4(\eta^2$-1,4-pentadiene) provides evidence that $HRu(CO)_3(\eta^3$-$C_5H_7)$ can be an intermediate in the isomerization of $Ru(CO)_3(\eta^4$-1,4-pentadiene) to $Ru(CO)_3(\eta^4$-1,3-pentadiene).

Scheme II. Photochemistry of $Ru(CO)_4(\eta^2\text{-diene})$ (diene = 1,4-pentadiene, 1,5-hexadiene, 1,6-heptadiene) and thermal reaction of $Ru(CO)_3(C_2H_4)_2$ and dienes in an alkane solution at 298 K.



We have demonstrated that $Ru(CO)_3(C_2H_4)_2$ is not only a catalyst for alkene isomerization[1] but serves as a "$Ru(CO)_3$" transfer reagent, permitting the synthesis of novel, thermally labile ruthenium complexes of acyclic non-conjugated dienes.

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Table I. IR Data for Relevant Complexes

species	medium (T, K)	ν, cm^{-1} (rel abs)
$Ru_3(CO)_{12}$	3MP[a] (298)	2061 (2.7), 2031 (1.6), 2012 (1.0)
$Ru(CO)_3(PPh_3)_2$	3MP (298)	1907
$Ru(CO)_3(C_2H_4)$[c]	3MP (55)	2055 (1.0), 1978 (1.2), 1972 (1.3)
$Ru(CO)_4(C_2H_4)$	3MP (298)	2104 (1.0), 2023 (17.2), 1996 (8.5)
$Ru(CO)_4(C_3H_6)$	3MP (298)	2100 (1.0), 2018 (10.6), 1991 (6.4)
$Ru(CO)_4(C_5H_{10})$	3MP (298)	2100 (1.0), 2018 (9.3), 1989 (5.8)
$Ru(CO)_4(\eta^2$-1,4-pentadiene)	3MP (298)	2101 (1.0), 2019 (9.5), 1994 (5.1)
	MCH[b] (298)	2101 (1.0), 2019 (10.7), 1993 (6.0)
	MCH (77)	2103 (1.0), 2020 (7.0), 1991 (5.4)
$Ru(CO)_4(\eta^2$-3-methyl-$C_5H_7)$[d]	3MP (298)	2101 (1.0), 2019 (9.1), 1993 (4.9)
$Ru(CO)_4(\eta^2$-1,5-hexadiene)	3MP (298)	2101 (1.0), 2019 (9.2), 1992 (5.0)
$Ru(CO)_4(\eta^2$-1,6-heptadiene)	3MP (298)	2100 (1.0), 2019 (9.6), 1992 (4.8)
$Ru(CO)_3(C_2H_4)_2$	3MP (298)	2081 (1.0), 2005 (7.1), 1995 (20.3)
$Ru(CO)_3(C_3H_6)_2$	3MP (298)	2075 (1.0), 2005 (3.3), 1988 (14.0)
$Ru(CO)_3(C_5H_{10})_2$	3MP (298)	2072 (1.0), 2005 (2.6), 1987 (9.4)
$Ru(CO)_3(\eta^2$-1,4-pentadiene$)_2$	MCH (77)	2077 (1.0), 2002 (3.0), 1994 (6.1)
$Ru(CO)_3(\eta^2$-1,6-heptadiene$)_2$	3MP (298)	2074 (1.0), 1998 (2.5), 1986 (9.8)
$Ru(CO)_3(\eta^4$-1,4-pentadiene)	3MP (298)	2050 (1.1), 1992 (1.0), 1966 (1.0)
	MCH (77)	2048 (1.0), 1992 (1.0), 1960 (1.1)
$Ru(CO)_3(\eta^4$-3-methyl-1,4-$C_5H_7)$[d]	3MP (298)	2052 (1.2), 1994 (1.1), 1968 (1.0)
$Ru(CO)_3(\eta^4$-1,5-hexadiene)	3MP (298)	2050 (1.1), 1994 (1.1), 1966 (1.0)
$Ru(CO)_3(\eta^4$-1,3-pentadiene)	3MP (298)	2063 (1.0), 1998 (1.6), 1987 (1.4)
$Ru(CO)_3(\eta^4$-3-methyl-1,3-$C_5H_7)$[e]	3MP (298)	2061 (1.0), 1996 (1.5), 1983 (1.4)
$Ru(CO)_3(\eta^4$-1,3-butadiene)[f]	Hexane (298)	2069 (s), 2006 (vs), 1995 (s)
$HRu(CO)_3(\eta^3-C_3H_5)$	MCH (77)	2082 (1.0), 2008 (1.2)
$HRu(CO)_3(\eta^3-C_5H_9)$	MCH (77)	2078 (1.0), 2004 (1.2)
$HRu(CO)_3(\eta^3-C_5H_7)$	MCH (77)	2080 (1.0), 2006 (1.2)

[a] 3MP = 3-methylpentane.
[b] MCH = methylcyclohexane.
[c] Band positions obtained from ref 1.
[d] 3-methyl-1,4-C_5H_7 = 3-methyl-1,4-pentadiene.
[e] 3-methyl-1,3-C_5H_7 = 3-methyl-1,3-pentadiene.
[f] Band positions obtained from ref 14.

Figure Captions

Figure 1. IR difference spectral changes accompanying thermal reaction of $Ru(CO)_3(C_2H_4)_2$ with 1,4-pentadiene in 3-methylpentane solution at 298 K (Δt = 60, 90, 120, 180 s). The positive peaks at 2050 and 1966 cm^{-1} are due to the intermediate $Ru(CO)_3(\eta^4$-1,4-pentadiene). The spectra were taken as the concentration of this intermediate was decreasing with time and isomerizing to $Ru(CO)_3(\eta^4$-1,3-pentadiene). The positive peaks at 2063, 1998, and 1987 cm^{-1} are due to this product.

Figure 2. (a) IR difference spectral changes accompanying thermal reaction of $Ru(CO)_3(C_2H_4)_2$ with 3-methyl-1,4-pentadiene in 3-methylpentane solution at 298 K (Δt = 30, 60, 90 s). The positive peaks at 2052 and 1968 cm^{-1} correspond to $Ru(CO)_3(\eta^4$-3-methyl-1,4-pentadiene). (b) IR difference spectral changes accompanying thermal isomerization of $Ru(CO)_3(\eta^4$-3-methyl-1,4-pentadiene) from (a) in 3-methylpentane solution at 298 K (Δt = 30, 60, 90 min). The positive peaks at 2061, 1996, 1983 cm^{-1} correspond to $Ru(CO)_3(\eta^4$-3-methyl-1,3-pentadiene).

Figure 3. (a) IR difference spectral changes measured ~1 min after a 50 μs flash photolysis of $Ru(CO)_4(\eta^2$-1,4-pentadiene) in 3-methylpentane solution containing ~1 M 1,4-pentadiene at 298 K. The positive peaks at 2050, 1992, and 1966 cm^{-1} correspond to $Ru(CO)_3(\eta^4$-1,4-pentadiene). (b) IR difference spectral changes accompanying thermal isomerization of $Ru(CO)_3(\eta^4$-1,4-pentadiene) from (a) in 3-

methylpentane solution at 298 K (Δt = 30, 60, 120 s). The positive peaks at 2063, 1998, and 1987 cm^{-1} correspond to $Ru(CO)_3(\eta^4$-1,3-pentadiene).

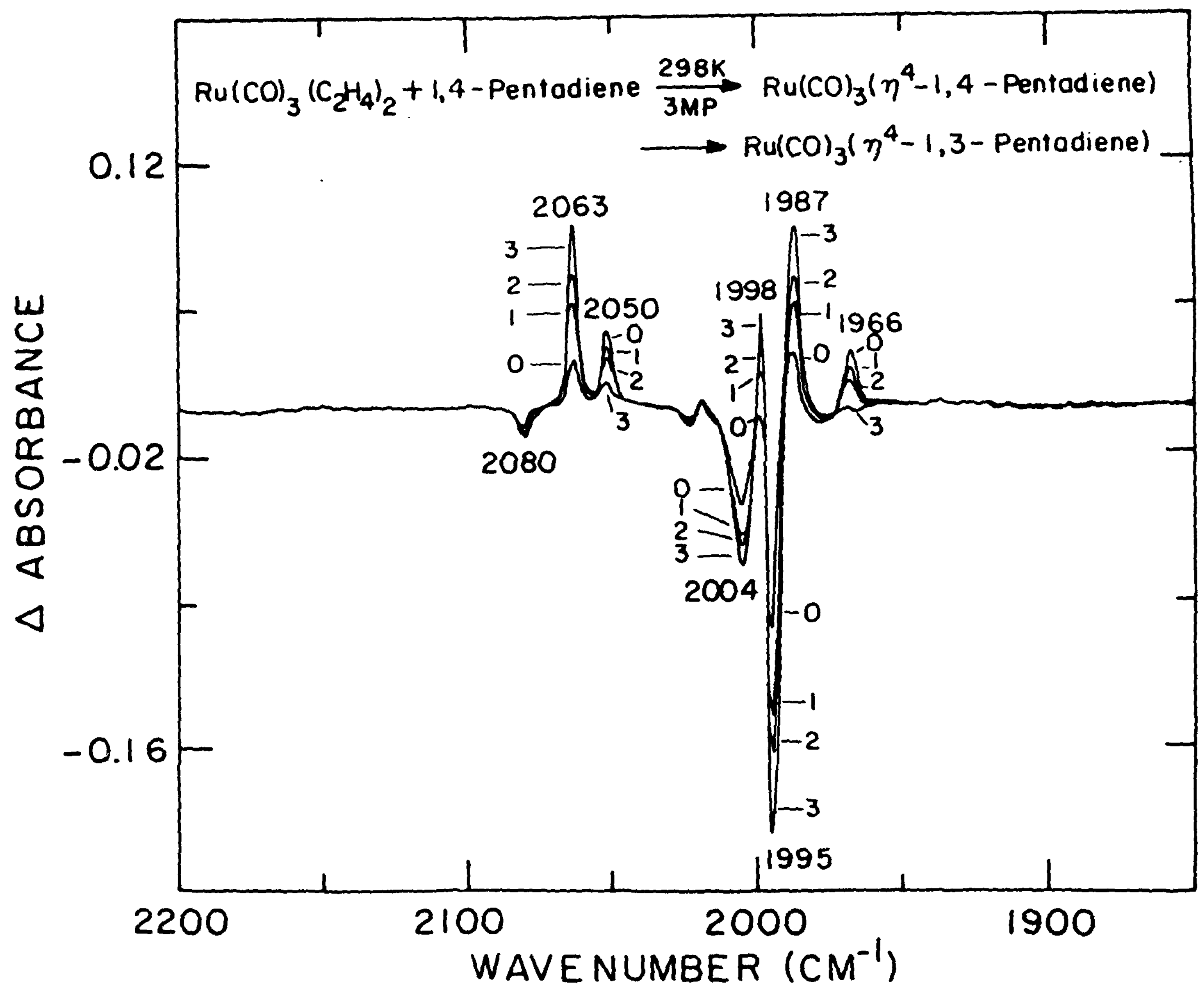
Figure 4. IR difference spectral changes due to near-UV irradiation of $Ru(CO)_4(\eta^2$-1,4-pentadiene) in a methylcyclohexane matrix containing ~1 M 1,4-pentadiene at 77 K. The positive peaks at 2048 and 1960 cm^{-1} are due to $Ru(CO)_3(\eta^4$-1,4-pentadiene), the peaks at 2080 and 2006 cm^{-1} are due to $HRu(CO)_3(\eta^3-C_5H_7)$, and the peak at 2132 cm^{-1} is due to free CO.

Figure 5. (a) IR difference spectral changes accompanying thermal reaction of $Ru(CO)_3(C_2H_4)_2$ with 1,5-hexadiene in 3-methylpentane solution at 298 K (Δt = 30, 60, 90 s). The positive peaks at 2050 and 1966 cm^{-1} correspond to $Ru(CO)_3(\eta^4$-1,5-hexadiene). (b) IR spectrum for $Ru(CO)_3(\eta^4$-1,5-hexadiene) after thermal reaction from (a) completed. The peak at 2019 cm^{-1} is due to trace amount of $Ru(CO)_4(\eta^2$-1,5-hexadiene).

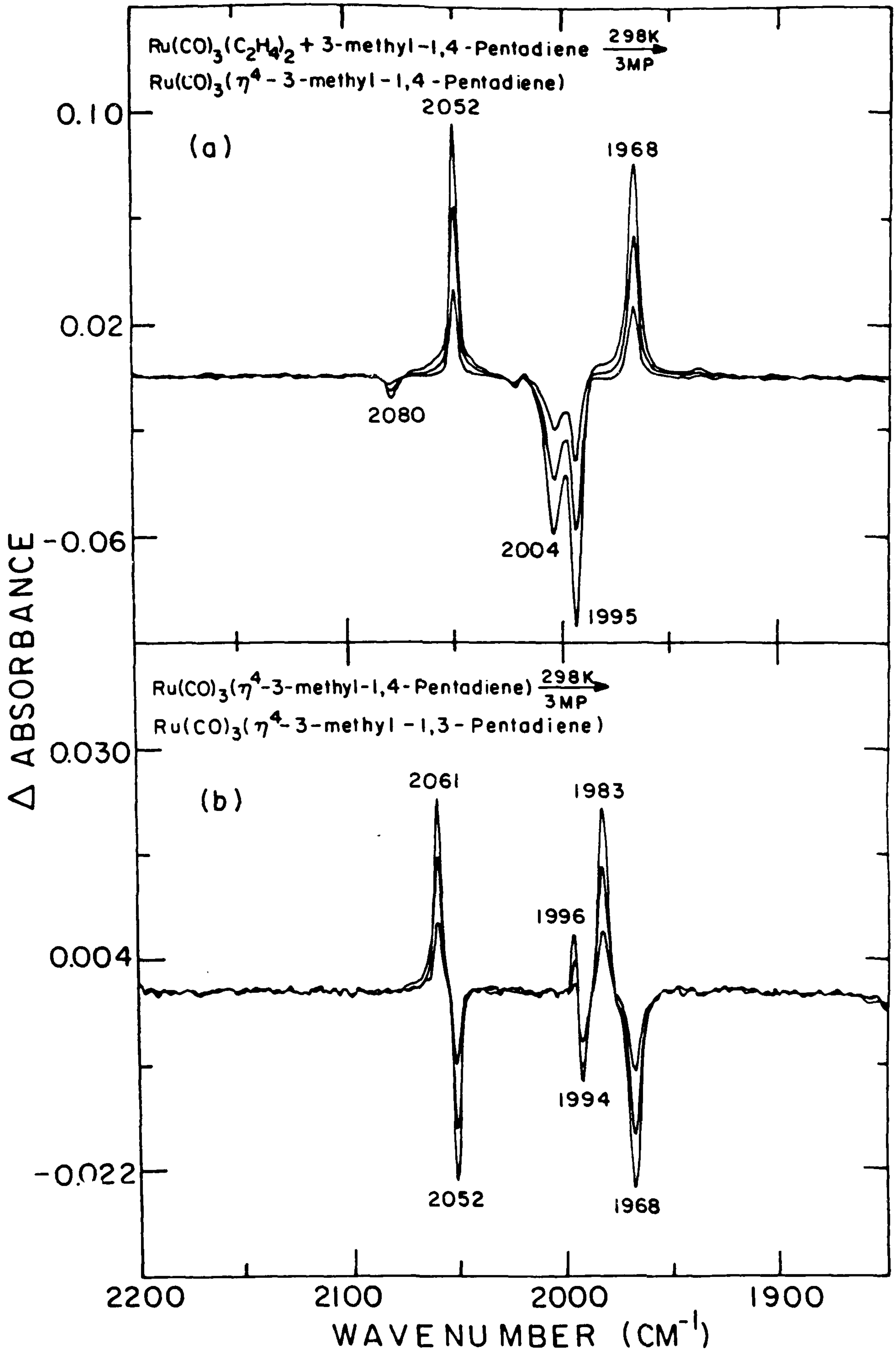
Figure 6. IR difference spectral changes measured ~1 min after a 50 μs flash photolysis of $Ru(CO)_4(\eta^2$-1,5-hexadiene) in a 3-methylpentane solution containing ~1 M 1,5-hexadiene at 298 K. The positive peaks at 2050 and 1966 cm^{-1} are due to $Ru(CO)_3(\eta^4$-1,5-hexadiene).

Figure 7. IR difference spectral changes accompanying thermal reaction of $Ru(CO)_3(C_2H_4)_2$ with 1,6-heptadiene in 3-methylpentane solution at 298 K (Δt = 30, 60, 90, 120 s). The positive peaks at 2074 and 1986 cm^{-1} correspond to

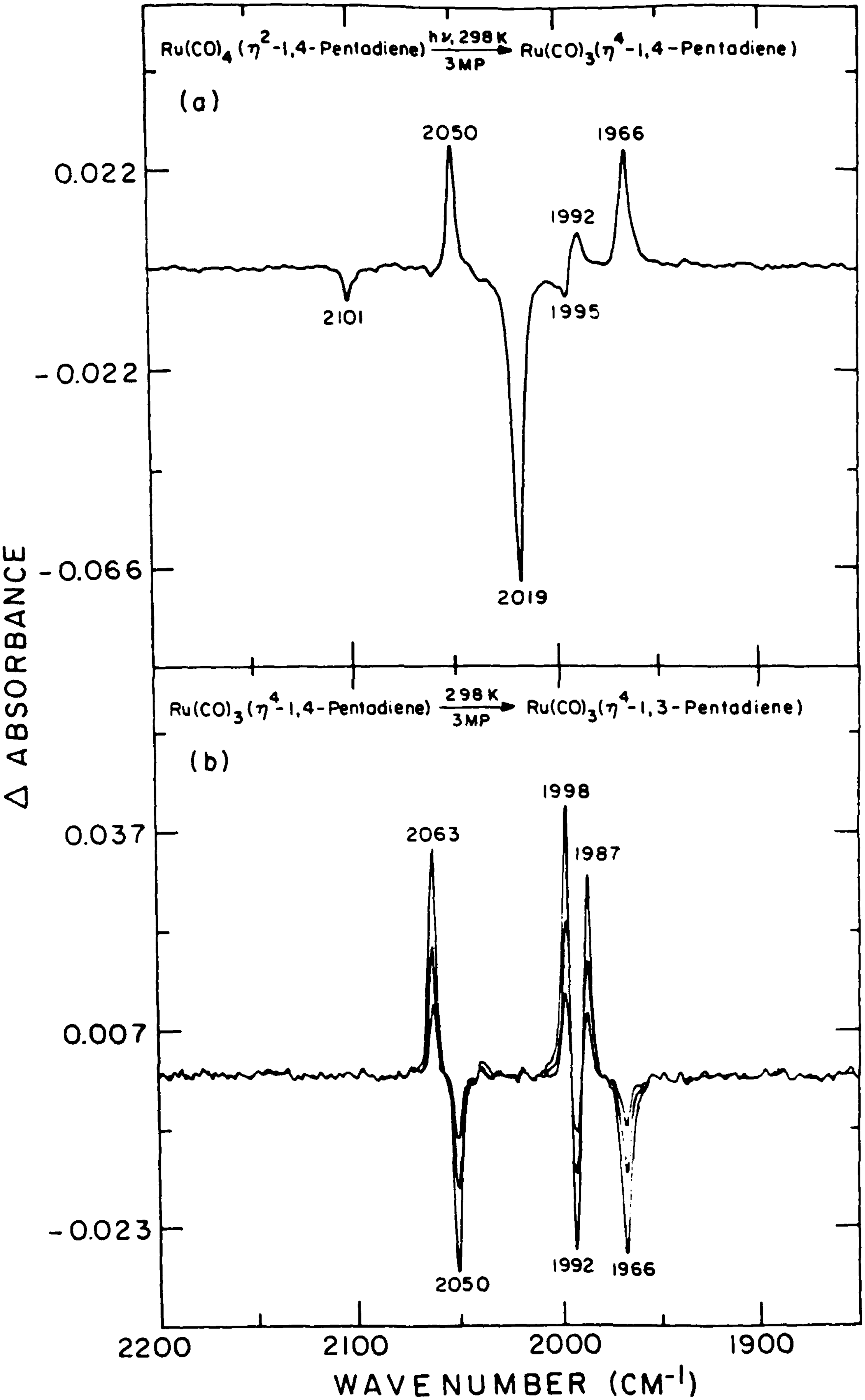
$Ru(CO)_3(\eta^2\text{-1,6-heptadiene})_2$.



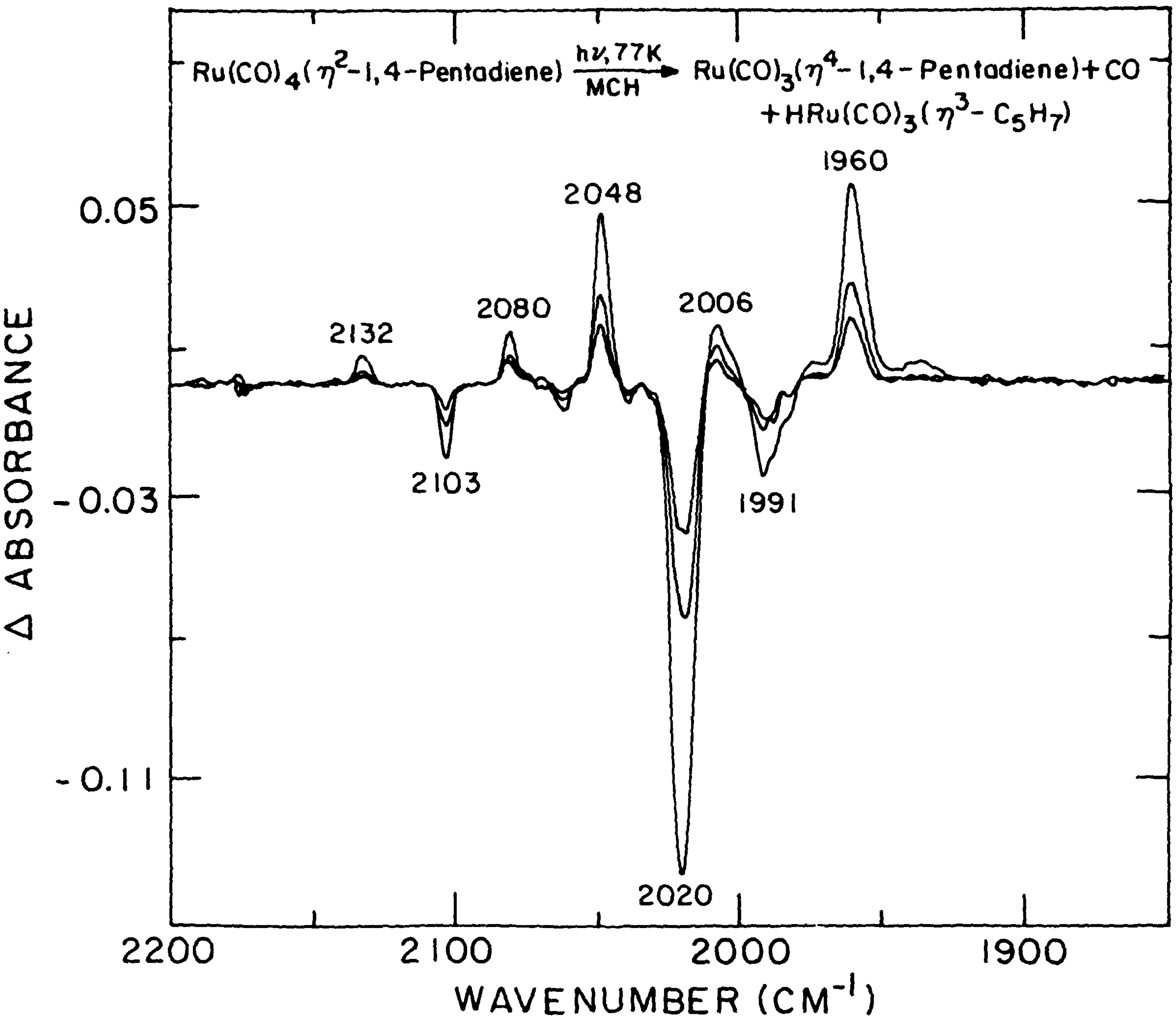
Ru(CO)3 (C2H4)2 + 1,4-Pentadiene
298K
3MP
Ru(CO)3(η4-1,4-Pentadiene)
Ru(CO)3(η4-1,3-Pentadiene)
0.12
-0.02
-0.16
Δ ABSORBANCE
2063
2050
2080
1998
2004
1987
1966
1995
2200
2100
2000
1900
WAVENUMBER (CM-1)



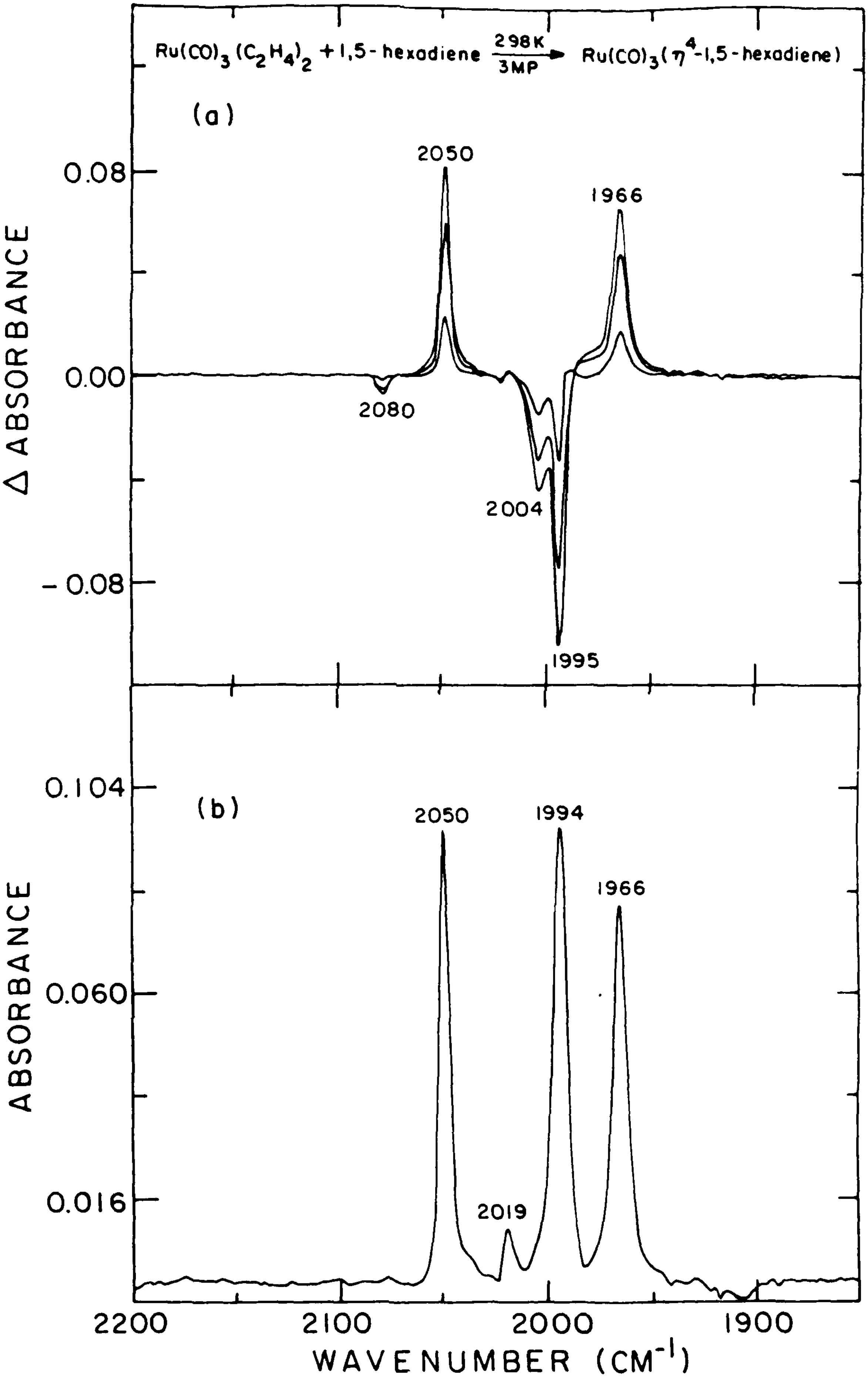
Ru(CO)3(C2H4)2 + 3-methyl-1,4-Pentadiene 298K 3MP
Ru(CO)3(η4-3-methyl-1,4-Pentadiene)
(a)
2052
1968
2080
2004
1995
Ru(CO)3(η4-3-methyl-1,4-Pentadiene) 298K 3MP
Ru(CO)3(η4-3-methyl-1,3-Pentadiene)
(b)
2061
1983
1996
1994
2052
1968
0.10
0.02
-0.06
0.030
0.004
-0.022
Δ ABSORBANCE
2200
2100
2000
1900
WAVENUMBER (CM-1)



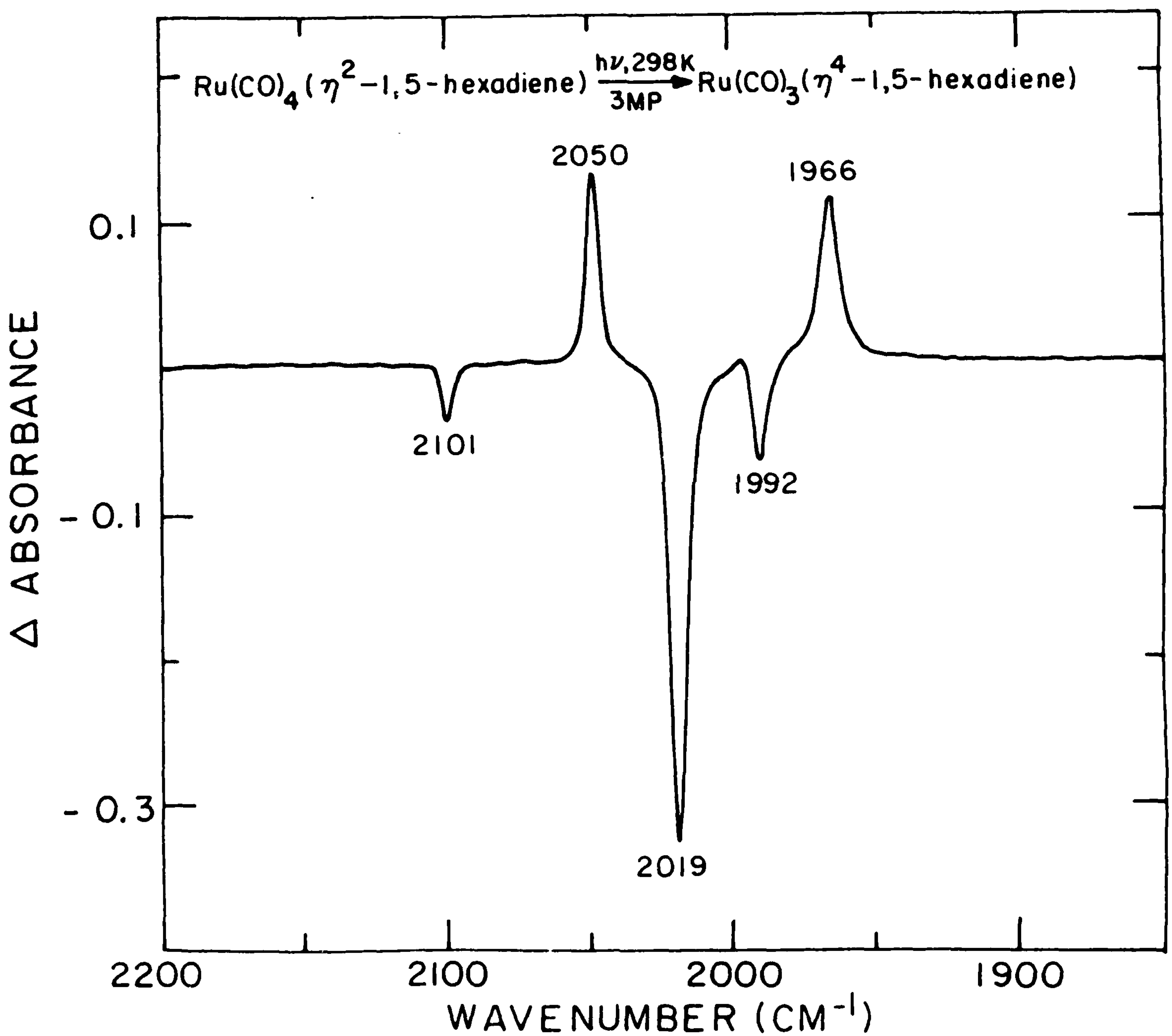
Ru(CO)4 (η2-1,4-Pentadiene) hν, 298 K / 3MP → Ru(CO)3(η4-1,4-Pentadiene)
(a)
2050
1966
1992
2101
1995
2019
Ru(CO)3(η4-1,4-Pentadiene) 298 K / 3MP → Ru(CO)3(η4-1,3-Pentadiene)
(b)
1998
2063
1987
2050
1992
1966
0.022
-0.022
-0.066
0.037
0.007
-0.023
Δ ABSORBANCE
2200
2100
2000
1900
WAVENUMBER (CM-1)



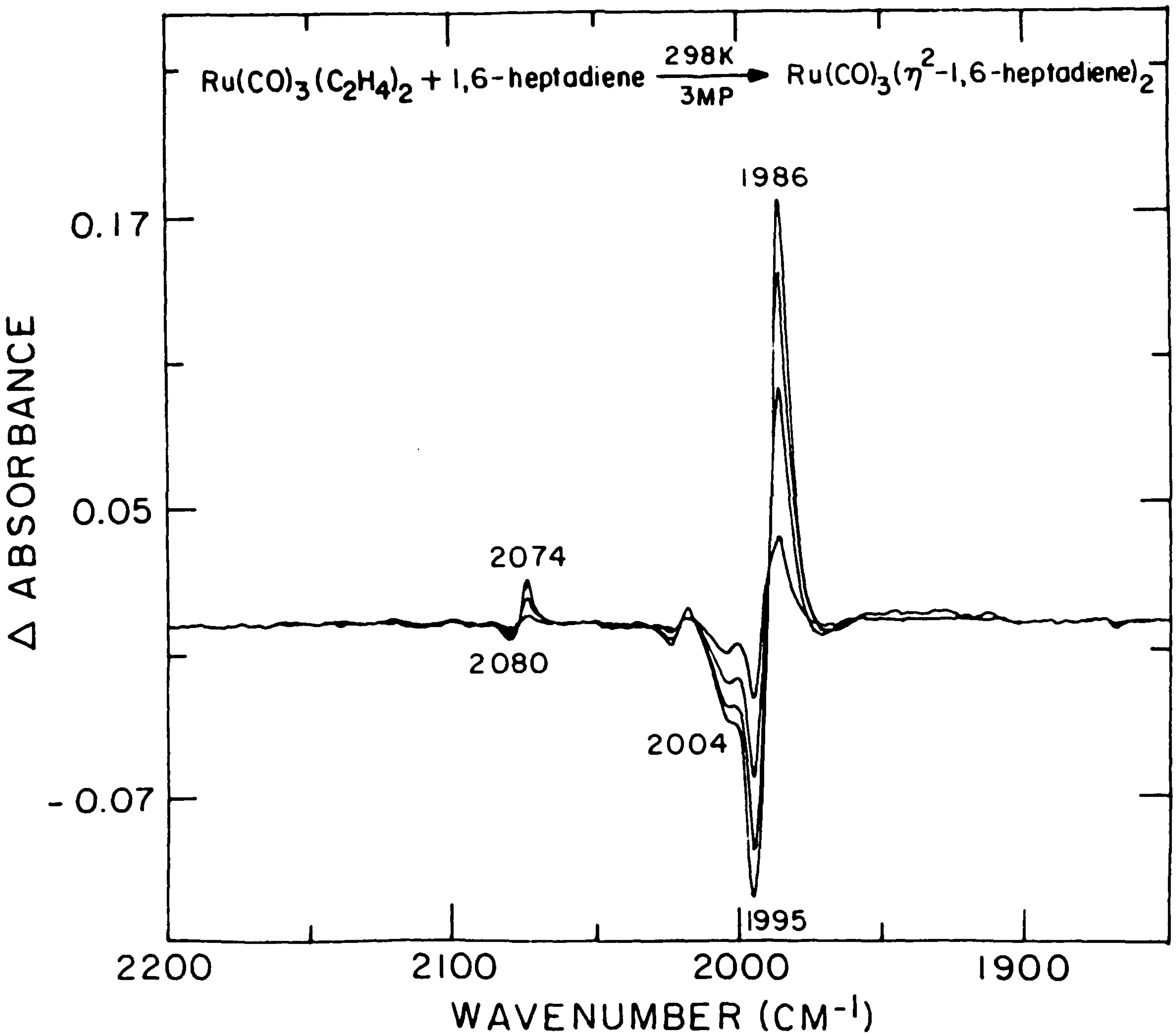
$Ru(CO)_4(\eta^2\text{-}1,4\text{-Pentadiene}) \xrightarrow[MCH]{h\nu, 77K} Ru(CO)_3(\eta^4\text{-}1,4\text{-Pentadiene}) + CO$
$+ HRu(CO)_3(\eta^3\text{-}C_5H_7)$
2132
2103
2080
2048
2020
2006
1991
1960
0.05
-0.03
-0.11
Δ ABSORBANCE
2200
2100
2000
1900
WAVENUMBER (CM^{-1})



Ru(CO)3(C2H4)2 + 1,5-hexadiene 298K 3MP Ru(CO)3(η4-1,5-hexadiene)
(a)
2050
1966
2080
2004
1995
0.08
0.00
-0.08
Δ ABSORBANCE
(b)
2050
1994
1966
2019
0.104
0.060
0.016
ABSORBANCE
2200
2100
2000
1900
WAVENUMBER (CM-1)



Ru(CO)4(η2-1,5-hexadiene) hν,298K 3MP Ru(CO)3(η4-1,5-hexadiene)
2050
1966
2101
1992
2019
0.1
-0.1
-0.3
Δ ABSORBANCE
2200
2100
2000
1900
WAVENUMBER (CM-1)



Ru(CO)3(C2H4)2 + 1,6-heptadiene
298K
3MP
Ru(CO)3(η2-1,6-heptadiene)2
1986
2074
2080
2004
1995
0.17
0.05
-0.07
Δ ABSORBANCE
2200
2100
2000
1900
WAVENUMBER (CM-1)

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